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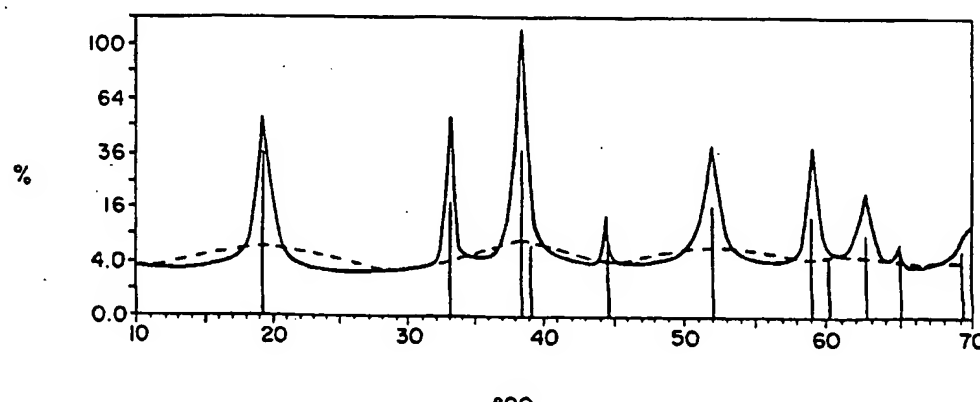
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(54) Title: NICKEL HYDROXIDE ACTIVE MATERIAL FOR ELECTRO CHEMICAL CELLS		
		
<p>(57) Abstract</p> <p>An alpha phase nickel hydroxide active material for use in the positive electrodes of rechargeable alkaline electrochemical cells in which the material comprises nickel and hydroxide constituents and first and second stabilizing cations. The first stabilizing cation is selected from the group comprising: Al, Co, La, Ce, Y, Nd, Mg, In and Mn. The second stabilizing cation is selected from the group comprising: Mg, Zn, Co, Sr, Y, Nd, La, Ce and In. The alpha phase material exhibits an increased discharge plateau voltage profile, is structurally stable and possesses multi-electron per nickel atom transfer capabilities. The higher discharge plateau voltage and improved storage capacity translates into a significant increase in specific energy density and power density in operating cells.</p>		

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**NICKEL HYDROXIDE ACTIVE MATERIAL
FOR ELECTRO CHEMICAL CELLS**

Background of the Invention

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This invention relates to active materials for use in the cathodes or positive electrodes of electrochemical cells and, in particular, to nickel hydroxide active material and cathodes or positive electrodes formed from
10 such nickel hydroxide active material.

Active material containing nickel hydroxide has long been used in the cathodes or positive electrodes of rechargeable or secondary batteries and, in particular, in alkaline rechargeable batteries. Typical batteries which
15 have used this material include nickel metal hydride, nickel cadmium, nickel hydrogen, nickel iron and nickel zinc.

The molecular structure of nickel hydroxide active material is well known. There are two phases of the
20 material, the alpha phase and the beta phase. Currently, the beta phase nickel hydroxide is most widely used in battery cathodes. The beta phase material is generally oxidized and reduced between the plus two and plus three oxidation states. Commercially available beta nickel
25 hydroxide exchanges 0.9 electrons per nickel atom.

The alpha phase nickel hydroxide is produced by driving the nickel to the plus four oxidation state. Due to this oxidation state, the alpha phase nickel hydroxide can exchange as high as 1.67 electrons per nickel atom for
30 thin film electrodes. This represents an 85 percent improvement in the electrode's storage capacity, as compared to an electrode using the beta phase material.

However, due to the instability of the alpha phase material, it is not currently used in commercial battery
35 electrodes. In spite of this, the possibility of realizing electrodes with a significantly higher overall storage capacity continues to drive researchers to develop a stabilized alpha material.

Several research efforts have resulted in alpha materials which are stable when exposed quiescently to potassium hydroxide of 5 to 8 molar concentration. However, the true test for stability is whether the material remains stable when subjected to repeated charging and discharging cycles at various rates. In most of the reported research, under these conditions, the alpha materials slowly develop an undesired secondary beta phase and the effect of multi-electron transfer is short lived.

Other research efforts have identified that partial substitution of the nickel cations with trivalent cations such as aluminum, cobalt or iron at greater than 20 wt. percent appears to stabilize the alpha phase structure of the double layered nickel hydroxide material. Some researchers have also purposely introduced various anions such as Cl^- , NO_3^- , CO_3^{2-} , or SO_4^{2-} along with the trivalent cation additions in order to evaluate the physical changes occurring within the brucite structure. It has been reported that using the trivalent aluminum cation in greater than 20 wt. percent along with the deliberate addition of the CO_3^{2-} anion could stabilize the alpha structure for reversible electrode applications.

While anions have been added to promote stability of the alpha phase nickel hydroxide, it is known in nickel battery technology that these anions also act as contaminants which are detrimental to battery performance. Thus, nitrates (NO_3^-) are known to promote self discharge of the positive electrode through the well known nitrate shuttle. In some specific applications, ternary electrolytes containing potassium carbonate have been found to reduce shape change of the zinc anode, but generally any carbonates are looked upon as being undesired. Chlorides and sulfates as well are viewed in various other battery systems as contaminants detrimental to the proper battery performance.

It is, therefore, an object of the present invention to provide an improved alpha phase nickel hydroxide

material having increased stability.

It is a further object of the present invention to provide a positive or cathode electrode using such improved alpha phase nickel hydroxide.

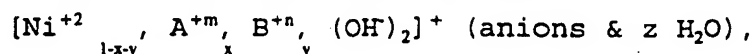
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Summary of the Invention

In accordance with the principles of the present invention, the above and other objectives are realized in
 10 a nickel hydroxide active material in which at least first and second stabilizing cations are included in the material with the nickel and hydroxide constituents, to promote greater charge imbalance. The first stabilizing cation can be a trivalent or divalent cation, but
 15 preferably it is a trivalent cation. The second stabilizing cation can also be a divalent or trivalent cation.

Preferably, the second cation is selected, with respect to its ionic radii and multi-valency, to promote
 20 charge imbalance in both the basal lamellar nickel plane and the interlamellar double oxygen layers. In the aforesaid preferred form, water and hydroxyl anions will be intercalated in between the oxygen double layers, assisting the second stabilizing cation in realizing
 25 complete stabilization.

In the preferred form of the invention, the nickel hydroxide active material has the general formula



30

where A is the first stabilizing cation and can be any divalent or preferably trivalent cation with an ionic radii of from 0.2 angstroms to 1.4 angstroms, where B is the second stabilizing cation and can be any divalent or
 35 trivalent cation with an ionic radii of from 0.2 angstroms to 1.4 angstroms, and z can be any fraction waters entrapped within the structure. More preferably, the A cation can be any cation specie selected from the group comprising Al, Co, La, Ce, Y, Nd, Mg, In and Mn, and the

B cation can be any cation specie selected from the group comprising Mg, Zn, Co, Sr, Y, Nd, La and Ce.

Detailed Description of the Drawings

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The above and other features and aspects of the present invention will become more apparent above reading the following detailed description in conjunction with the accompanying drawings, in which:

10 FIG. 1 shows an X-ray diffraction scan of a commercially available beta phase nickel hydroxide material;

15 FIG. 2 shows an X-ray diffraction scan of both a commercially available beta phase nickel hydroxide material and an alpha phase nickel hydroxide material in accordance with the principles of the present invention;

20 FIGS. 3 and 4 illustrate X-ray diffraction scans of alpha phase nickel hydroxide materials in accordance with the principles of the present invention, and having first and second stabilizing cations selected from a first group of stabilizing cations;

25 FIGS. 5 and 6 illustrate X-ray diffraction scans of alpha phase nickel hydroxide materials in accordance with the principles of the present invention, and having stabilizing cations selected from a second group of stabilizing cations;

30 FIGS. 7-10 show X-ray diffraction scans of alpha phase nickel hydroxide materials in accordance with the principles of the present invention, and having first and second stabilizing cations selected from a third group of stabilizing cations;

35 FIG. 11 shows an x-ray diffraction scan of an alpha phase nickel hydroxide material in accordance with the principles of the present invention, and having first and second stabilizing cations selected from a fourth group of stabilizing cations;

FIG. 12 shows a thermogravimetric analysis profile of a commercially available beta phase nickel hydroxide

material;

FIGS. 13 and 14 illustrate thermogravimetric gas analysis profiles of alpha phase hydroxide materials in accordance with the principles of the present invention;

5 FIG. 15 shows infra-red spectra of alpha phase hydroxide materials in accordance with the principles of the present invention;

FIGS. 16 and 17 show partial and full discharge cycles, respectively, of an electrochemical cell using a zinc negative electrode and a nickel positive electrode formed from a standard beta phase nickel hydroxide material;

FIGS. 18 and 19 show partial and full discharge cycles, respectively of an electrochemical cell using a zinc negative electrode and a nickel positive electrode formed from an alpha phase nickel hydroxide material in accordance with the principles of the present invention;

15 FIG. 20 illustrates a structural diagram of an alpha phase nickel hydroxide material in accordance with the principles of the present invention; and

FIG. 21 shows is a brucite structure of a standard commercially available beta phase nickel hydroxide material.

Detailed Description

25

In accordance with the principles of the present invention, in a preferred form of the invention, beta phase nickel hydroxide active material having multiple stabilizing cations is provided having the general formula

30 $[Ni^{+2}_{1-x}, A^{+m}_x, B^{+n}_y, (OH)_2]^+ (anions \& z H_2O),$

where A is a first stabilizing cation and can be any divalent or, preferably, trivalent cation with an ionic radii of from 0.2 angstroms to 1.4 angstroms, where B is a second stabilizing cation and can be any divalent or trivalent cation with an ionic radii of from 0.2 angstroms to 1.4 angstroms and z can be any fraction waters entrapped within the structure. Preferable materials for

the A cation can be any cation material selected from the group comprising Al, Co, La, Ce, Y, Nd, Mg, In and Mn. Preferable materials for the B cation can be any cation material selected from the group comprising Mg, Zn, Co, Sr, Y, Nd, La and Ce.

Nickel hydroxide alpha phase materials having the above attributes have been fabricated. The fabricated materials were grouped into four groups identified as Groups I, II, III and IV, with the materials in each group having similar characteristics for their A and B cations.

In the Group I materials, the A stabilizing cation had a smaller ionic radii than nickel. The B stabilizing cation was either a divalent or trivalent cation having an ionic radii larger than nickel.

In the Group II materials, the A stabilizing cation was a trivalent cation having an ionic radii similar to nickel. The B stabilizing cation was either a divalent or trivalent cation having a radii within a range of radii.

In the Group III materials, the A cation was either a divalent or higher multi-valent cation having ionic radii which tended to be larger than nickel. The B cation was a trivalent cation with similar ionic radii.

In the Group IV materials, the A cation had the ability to reflect higher than trivalency and a radii very close to that of nickel. The B cation had valencies ranging from +2 to +3 and a radii also very close to that of nickel.

The materials in these groups were all subjected to X-ray diffraction ("XRD") analysis and the materials exhibited typical XRD patterns and broadened peaks identifying the materials as alpha phase nickel hydroxides. A typical scan is shown by the A scan in FIG. 2 and is compared to the XRD pattern of a typical beta phase nickel hydroxide material shown by the B scan in this figure. FIG. 1 shows the latter scan of the beta phase material alone.

FIGS. 3 and 4 illustrate the XRD patterns of representative Group I materials. These patterns

demonstrate that the analyzed materials are stabilized alpha phase nickel hydroxide. Similar XRD patterns exhibiting stabilized alpha material nickel hydroxide are shown in FIGS. 5 and 6 for representative Group II materials. XRD patterns for representative Group III materials are shown in FIGS. 7-10. These materials exhibited varying degrees of X-ray amorphous behavior with the material in FIG. 10 exhibiting complete X-ray amorphous behavior. FIG. 11 shows the XRD pattern for a representative Group IV material. It too shows a stabilized alpha nickel hydroxide material.

The above-mentioned XRD scans were carried out using a Phillips Norelco model 3720 X-ray Diffractometer employing the standard Ni filtered Cu $\text{K}\alpha_1$ radiation at 1.541 angstroms. Lattice parameters were compared with the JCPDS indices file.

The process for preparing the nickel hydroxide active materials in each of the Groups I-IV was similar. The process involved chemical precipitation of alpha nickel hydroxide using mixed metal nitrate solutions.

More particularly, each metal nitrate solution utilized from 1.3 to 1.6 molar concentration of reagent grade nickel nitrate. Each solution also contained at least one A cation selected from the aforementioned A cation group, i.e., from Al, Co, La, Ce, Y, Nd, Mg, In and Mn in from 0.3 to 0.6 molar concentrations (12% to 25% by wt.). A cation from the B cation group in from 0.05 to 0.3 molar concentration (3.0% to 20% by wt.) was additionally included in each solution. The B cation group, as also indicated above, contained the following materials: Mg, Zn, Co, Sr, Y, Ne, La, Ce, and In.

The precipitation process was initiated by a slow drop wise titration of one liter of a two molar metal nitrate solution into 2 liters of a four molar ammonium hydroxide solution stirred at a high rate. The drip rate of the metal nitrate solution was adjusted for 0.7 mls/min. The entire precipitation process encompassed four days from start to finish and the slow drop wise

titration was carried out over the first 24 hours.

After the titration ended, the ammonium hydroxide solution was allowed to stir at a high rate for an additional 24 hours, at a constant slightly elevated
5 temperature of 30°C, to facilitate nucleation and slow growth. Then the cover was removed from the heavy duty beaker and the ammonia was allowed to evaporate for another 36 hours with the same vigorous stirring.

The initial Ph of the ammonium hydroxide solution was
10 approximately 11. As the metal nitrate solution was added drop wise, it was complexed by the ammonia. It was observed that different cation additives impart certain colors or hues to the solution. Through gentle heating action, the ammonium complex decomposes and metal
15 hydroxide nucleation sites begin to form. As precipitation occurs, the Ph of the solution falls and the additives will precipitate out with the nickel hydroxide but not as an ideal homogeneous precipitate within the nickel hydroxide particle. The nickel hydroxide particles
20 are a mosaic with their respective additives.

The precipitation and particle growth occurs slowly over a period of 48 hours. The final Ph was approximately 9. At the end of the 84 hour process, the precipitate was allowed to rest in its mother liquid for approximately 12
25 hours. This allowed the precipitate to settle out so that the mother liquid could easily be decanted. The precipitate was then filtered using ultrafine retention paper and rinsed or washed to a neutral Ph. The nickel hydroxide material was then dried in a forced air
30 convection oven for approximately 6 hours at a temperature of 60°C. After drying, the nickel hydroxide was crushed and then sieved to minus 270 size. All over-sized material is recrushed and sieved again to completeness.

It was found that minor adjustments to the
35 precipitation process could be made to produce active material with distinct crystallite sizes from 28 angstroms to 131 angstroms.

A TGA analysis was performed on various alpha nickel

hydroxide materials fabricated as above-described. This analysis was conducted using a Dupont model 951 Thermogravimetric Analyzer. FIG. 12 is a TGA profile of a standard commercially available beta phase nickel hydroxide material and FIG. 13 is a TGA profile of a representative alpha nickel hydroxide material. As can be seen in FIG. 13, a two step profile weight loss occurs, whereby the first step observed is attributed to interlayer water loss, and the second step to dehydroxylation of the various anion contents and its subsequent loss as well. The second cation of the stabilized alpha nickel hydroxide of the invention promotes significant charge imbalance so that more water is entrapped in the intermellar regions improving structural stabilization. The magnitude of the two step profile of another representative alpha phase nickel hydroxide material in FIG. 14 confirms that more water is entrapped in this region.

The IR spectra for representative alpha nickel hydroxide materials were recorded using a Perkin-Elmer Model 1760-X Research FT-IR Spectrometer. Due to the interaction between various anions particularly nitrates contained within the fabricated active materials and the KBr pelletizing method of preparing these materials, two sets of materials for each cation combination were prepared. One set of active materials was prepared following the standard method. The second set of materials was prepared using a diluted KBr mixture. FIG. 15 shows IR signatures, identified as A-F, of six selected active alpha nickel hydroxide materials. These IR signatures are recognized to be characteristic of stabilized alpha nickel hydroxide. FIG. 15 also shows two further IR signatures identified as G-H, of standard commercially available beta nickel hydroxide materials for comparison with the IR signatures of the stabilized alpha nickel hydroxide materials.

Electrode material was prepared using the stabilized alpha nickel hydroxide active material fabricated as

above-described, following the patented plastic bonded process described in U.S. Patent 4,976,904. The alpha nickel hydroxide active material was dry mixed with Timcal electrolyte graphite of approximately 10 micron average particle size. A polytetrafluoroethylene (PTFE) binder was added along with a specific amount of medium aliphatic naphtha solvent. The ingredients were thoroughly mixed in a high-speed binder for 3 to 5 minutes.

The solvent was separated from the paste via vacuum extraction means. The electrode material, having the consistency of wet clay, was then mechanically worked fibrillating the PTFE binder. The electrode material was processed into sheets and placed on racks in a low heat medium airflow oven. The electrode sheets were allowed to dry for 48 hours before being processed into 2 ampere-hour size standard positive electrodes.

Selected electrodes were pre-formed and cycled between pure nickel counter electrodes, in a tri-electrode stack configuration. This test stack was placed in a polypropylene case and initially compressed to 90% of the static measured stack thickness by using small Plexiglas shims. A 35 wt. solution of KOH was poured into each cell case fully submerging the test stack. The cells were placed under 27 inches of vacuum for approximately one hour. After vacuum, the cells were allowed to rest for 16 hours (overnight) in a covered condition. Preformation and evaluation cycling was carried out with the test cells covered by parafilm to reduce the CO₂ take up otherwise realized if not covered.

The initial formation charge was 200% of theoretical capacity based on 1.5 e/ni transfer. The second through the fourth formation charge cycles were to 150% of the same theoretical capacity. All discharge rates were C/10 to zero volts as references to a Hg/HgO electrode. After this pre-formation testing, the electrodes were removed from the test stack, rinsed in deionized water and dried. The electrodes were then mated with zinc electrodes formulated for the expected capacity keeping the n to p

ratio at the standard value. Three full formation cycles were completed on each tri-electrode cell. The cells were then tested using C/10 charge and discharge rates with 15 percent overcharge based on the expected capacity at 1.5 e/n_i transfer.

Cell formation and capacity evaluation tests were performed using an Arbin Instruments multi-channel computer controlled cycler model BT-6008. FIGS. 16 and 17 show partial and full discharge voltage profiles from a standard Ni-Zn trielectrode test cell. FIGS. 18 and 19 show partial and full discharge voltage profiles of the cell of the invention which exhibits two distinct plateaus.

As can be seen from FIGS. 18 and 19, the first discharge plateau was at least 100 millivolts higher than the standard discharge voltage plateau observed with standard Ni-Zn cell. This first discharge plateau flattens out at above 1.8 volts, under load, and lasts for better than six of the more than nine hours of discharge before transitioning through 1.7 volts. The second discharge voltage plateau, having approximately the same slope, transitions from 1.56 volts to 1.48 volts over a period of three hours before the final knee. The discharge is terminated when the cell reaches the standard 1.2 volt limit.

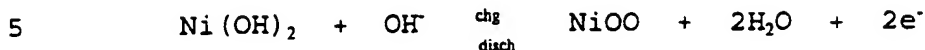
The first plateau is believed to be a combination of tetravalent and trivalent nickel being reduced to its divalent state. The second plateau is believed to be the remaining trivalent nickel reducing to the divalent state. This voltage profile is similar to the double plateau discharge profile of silver oxide zinc couples in which the silver discharges through argentic and argentous valence states.

The cathode reactions of the standard cathode electrode and the cathode electrodes of the invention are as follows:

Standard cathode electrode



Cathode of the Invention



The single electrode cell of the invention had a theoretical capacity of 2.97 ampere-hours based on calculations using the 1.5 electron per nickel atom value.
 10 The cell capacity for this discharge rate, ten cycles after cell formation, was measured at 2.72 ampere-hours. A single electrode cell having the same mass of active material and approximately the same physical dimensions using standard commercial grade beta nickel hydroxide
 15 material with the same paste formulation has a nominal capacity of 1.97 ampere-hours.

The alpha hydroxide materials of the invention have demonstrated an electron exchange of 1.38 electrons per nickel atom and a higher discharge plateau voltage during
 20 discharge cycles. The gravimetric utilization of this material is 0.390 amp-hrs per gram. Standard commercially available nickel hydroxide active material exhibits an electro-chemical utilization of approximately 0.275 amp-hr per gram. With a higher discharge plateau voltage and
 25 higher gravimetric active material energy density, batteries made with the alpha material of the invention have significantly higher specific energy densities.

Using the standard free energy E° of the standard Ni-Zn couple (1.73 volts) and on the basis of 100%
 30 utilization of the active material in both cathode and anode, the standard system has a theoretical specific energy density of 334 wh/kg. Observing the voltage discharge profile of FIG. 18, the first plateau after the knee is at 1.835 volts. Using the measured cathode
 35 gravimetric energy density of 0.390 Amp-hours per gram and the theoretical zinc anode gravimetric energy density of 0.658 Amp-hours per gram, one can calculate the theoretical specific energy density of a Ni-Zn battery

using the alpha material of the invention as $0.390 \text{ amp-hr/g} \times 0.658 \text{ amp-hr/g} \times 1.83 \text{ volts} \times 1000 = 471 \text{ watt-hours/kg}$. This represents a specific energy density improvement of 40 percent. Since the practical energy
5 density of a NiZn cell is presently 60 to 70 wh/kg, a real improvement to 85 to 100 wh/kg is possible with the positive electrode alpha materials of the invention.

FIG. 19 shows the structural diagram of the alpha nickel hydroxide material of the invention. This figure
10 depicts a brucite like structure that is elongated in the c lattice direction which is characteristic of the alpha structure. The c lattice parameter ranges from 8.8 angstroms to 9.5 angstroms. It is this elongation of the c lattice parameter that allows the second hydrogen atom
15 to be removed thereby forcing the nickel cation into a higher oxidation state and multi-electron transfer to occur.

FIG. 20 is the brucite structure of standard commercially available nickel hydroxide. The c lattice
20 parameter of standard beta material is 4.6 angstroms to 4.7 angstroms.

Table 1 below shows the capacities (theoretical and measured) of various electrodes made with the alpha phase nickel hydroxide of the invention. These capacities are
25 compared to the capacities (nominal) of equivalent electrodes made with standard commercially available beta phase nickel hydroxide. Table 1 also shows the similar characteristics (theoretical and measured) of an electrochemical cell made with the alpha phase positive
30 electrode of the invention, as compared to such a cell (nominal) made with standard commercially available beta phase nickel hydroxide. The increased capacity resulting from the alpha phase material is evident.

35

TABLE 1

Trielectrode	nominal capacity based on 0.9 e/ni	theoretical capacity based on 1.5 e/ni	measured capacity	e/ni
#1 E-1	1.97 amp-hrs	2.97 amp- hrs	2.72 amp-hrs	1.38
#2 E-2	1.37 amp-hrs	2.06 amp- hrs	1.85 amp-hrs	1.35
#3 E-3	2.53 amp-hrs	3.80 amp- hrs	3.21 amp-hrs	1.27
#4 E-4	1.82 amp-hrs	2.74 amp- hrs	2.06 amp-hrs	1.13
#5 Cell 1	8.0 amp- hrs	12.02 amp- hrs	10.64 amp-hrs	1.33

10

In all cases it is understood that the above-described arrangements are merely illustrative of the many possible specific embodiments which represent applications of the present invention. Numerous and varied other arrangements can be readily devised in accordance with the principles of the present invention without departing from the spirit and scope of the invention. Examples would be any other types of electrochemical storage devices, incorporating a cathode containing the positive alpha phase nickel hydroxide active material of the invention. Typical storage devices might be Nickel Metal Hydride, Nickel Iron, Nickel Hydrogen, Nickel Zinc, Nickel Manganese Oxide or Nickel Cadmium battery systems. Also, electrodes made with the alpha phase nickel hydroxide active material can additionally include spinel coated graphite in weight percent of 10 to 30 wt.% and cobalt hydroxide and/or cobalt suboxide powders in weight percent of from 1 to 4 wt.%.

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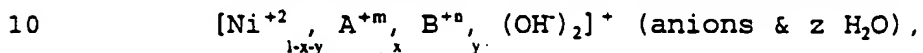
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What is Claimed is:

1. An alpha phase nickel hydroxide active material for use in a positive electrode of an electrochemical cell, said alpha phase nickel hydroxide material comprising nickel and hydroxide constituents and at least first and second different stabilizing cations.

2. An alpha phase nickel hydroxide active material in accordance with claim 1 wherein:

said material has the general formula



where A is any divalent or preferably trivalent cation with an ionic radii of from 0.2 to 1.4 angstroms, B is any divalent or trivalent cation with an ionic radii of from 0.2 to 1.4 angstroms, and z is any fractional waters entrapped within the material.

3. An alpha phase nickel hydroxide active material in accordance with claim 2 wherein:

the A cation and the B cation are selected with respect to their valency to maximize the overall charge imbalance condition for the material.

4. An alpha phase nickel hydroxide active material in accordance with claim 2 wherein:

the A cation and the B cation are selected with respect to their ionic radii and valency to maximize the overall charge imbalances of the lamellar region of the material, including creating hydroxyl vacancies resulting in charge imbalances in the interlamellar regions of the material.

5. An alpha phase nickel hydroxide active material in accordance with claim 2 wherein:

said A cation and B cation are selected to create a charge imbalance sufficient to entrap waters of hydration in the material, including the interlamellar regions of the material, thereby adding to stabilization of the material.

6. An alpha phase nickel hydroxide active material

in accordance with claim 2 wherein:

said A cation is selected from the group comprising: Al, Co, La, Ce, Y, Nd, Mg, In and Mn; and

said B cation is selected from the group
5 comprising: Mg, Zn, Co, Sr, Y, Nd, La, Ce and In.

7. An alpha phase nickel hydroxide active material in accordance with claim 6 wherein:

said material is precipitated from a mixed metal nitrate, sulfate or acetate homogeneous salt solution
10 containing said A cation in from 0.3 to 0.6 molar concentrations (12% to 25% by wt.) and said B cation in from 0.05 to 0.3 molar concentrations (3.0% to 20% by wt.).

8. An alpha nickel hydroxide active material in
15 accordance with claim 7 wherein:

an ammonia, or ammonia water or a nitrate, sulfate or acetate solution of ammonia is used as a precipitation control agent.

9. An alpha nickel hydroxide active material in
20 accordance with claim 8 wherein:

the metal nitrate solution is added to the ammonical solution in such a manner as to ensure complete dispersion and droplet micronization.

10. An alpha nickel hydroxide active material in
25 accordance with claim 8 wherein:

the molar ratio of metal salt solution to ammonical solution is adjusted to produce a mosaic mixed metal hydroxide material.

11. An alpha metal hydroxide material in accordance
30 with claim 10 wherein:

the molar and volume ratio of the metal salt solution to ammonical solution is adjusted to produce specific crystallite sizes and surface areas for the mosaic mixed metal hydroxide material.

35 12. A positive electrode comprised of the alpha phase nickel hydroxide active material as set forth in any one of claims 1 through 11.

13. The positive electrode of claim 12 further

comprising:

spinel coated graphite in weight percent of from 10 to 30 wt.% and cobalt hydroxide and/or cobalt suboxide powders in weight percent from 1 to 4 wt.%.

5 14. A nickel-zinc cell comprising the positive electrode claimed in claim 12.

15. An alpha phase nickel hydroxide active material in accordance with claim 1 wherein:

10 said material exhibits an improved discharge plateau and an improved electrochemical utilization in the range of 1.3 to 1.5 electrons per nickel atom.

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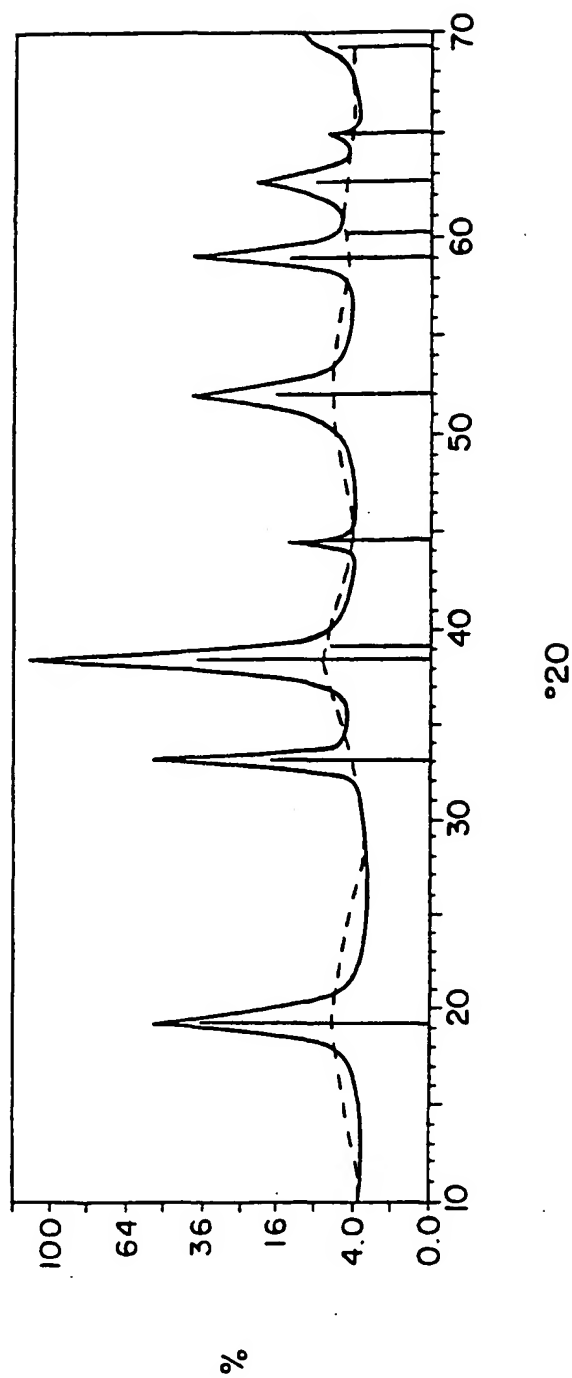
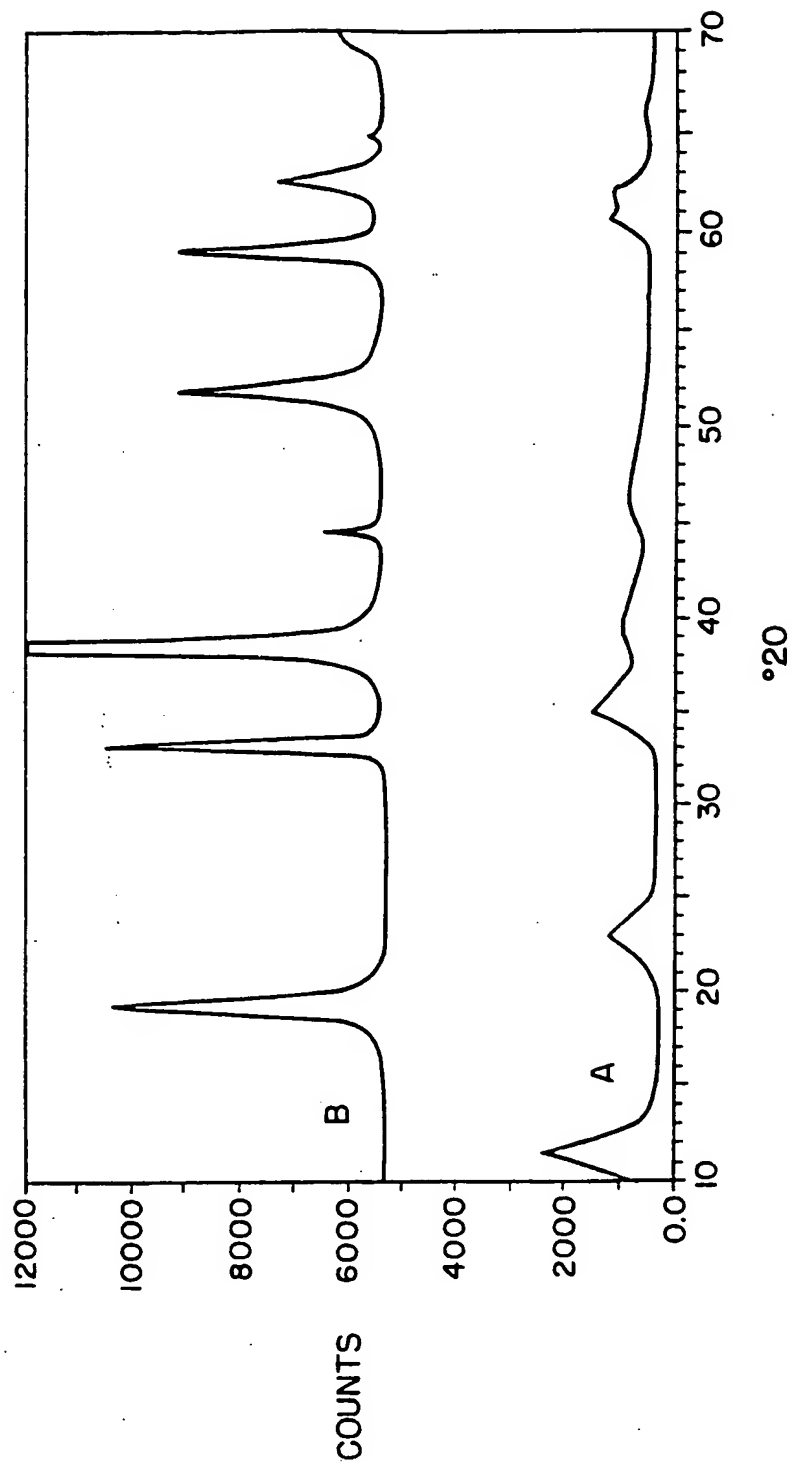


FIG. 1

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*FIG. 2*

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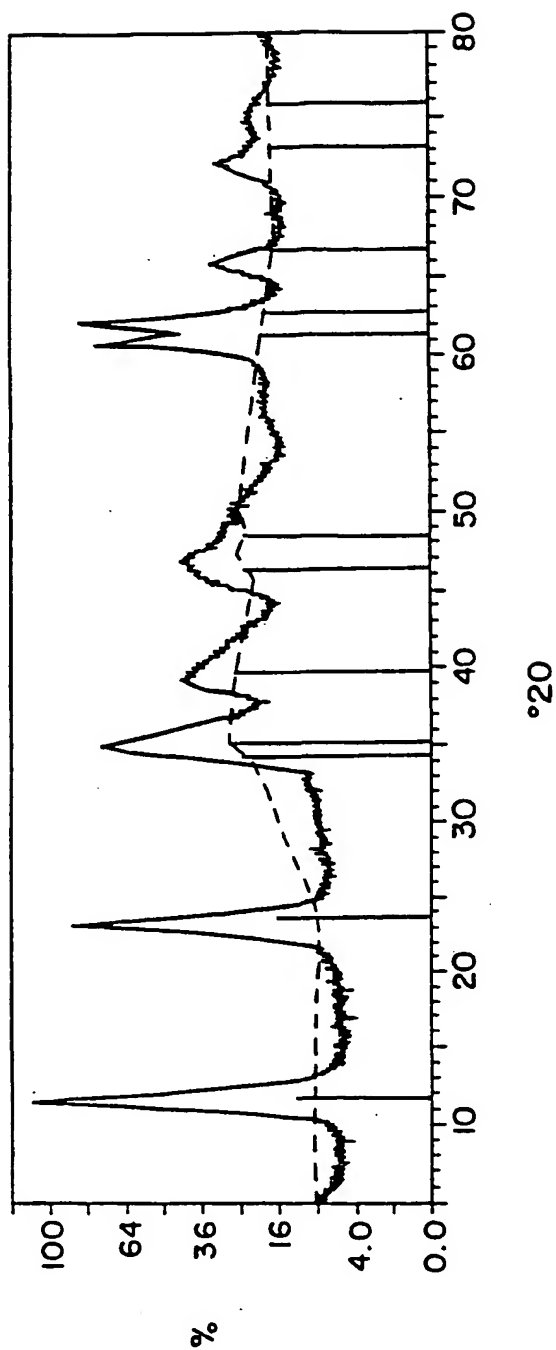


FIG. 3

4721

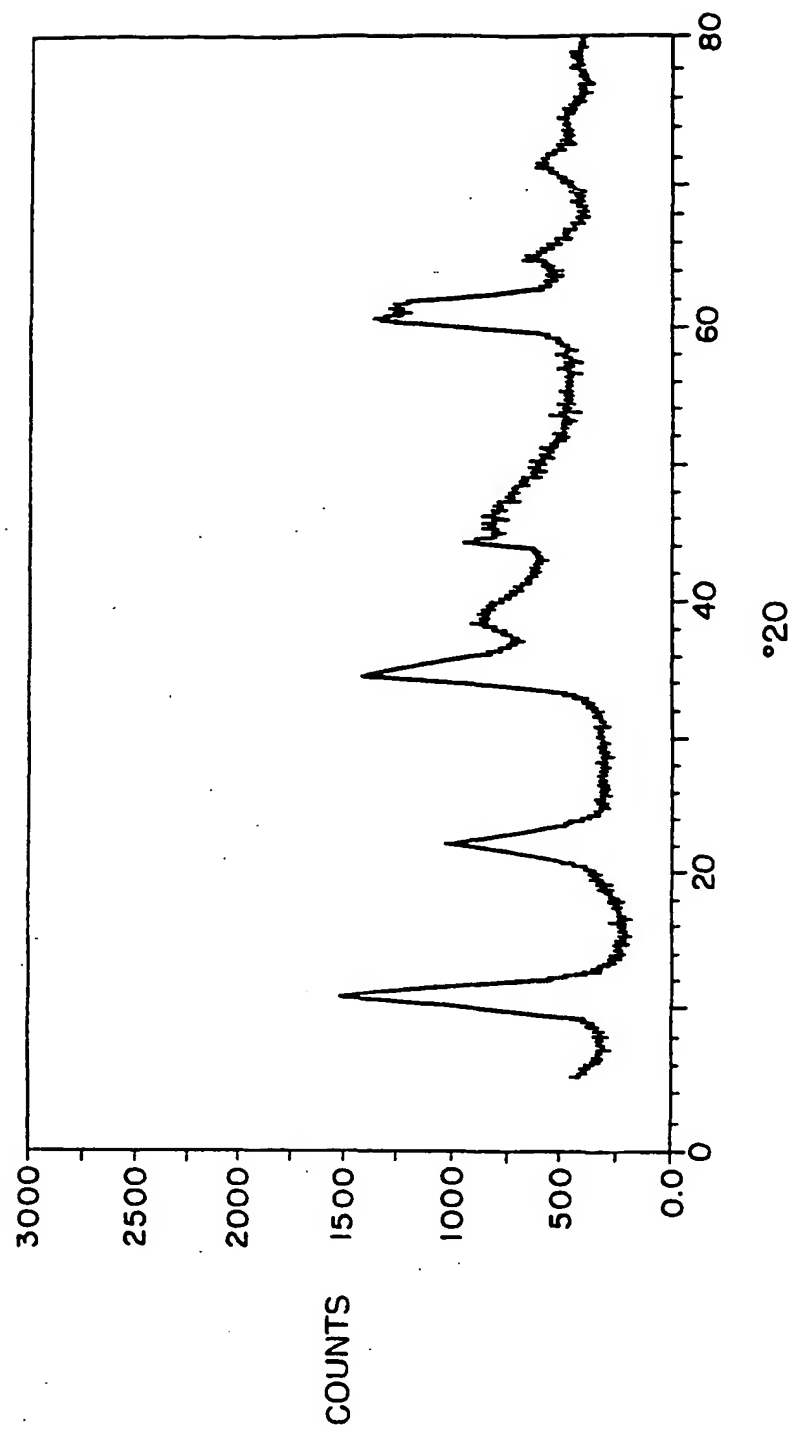


FIG. 4

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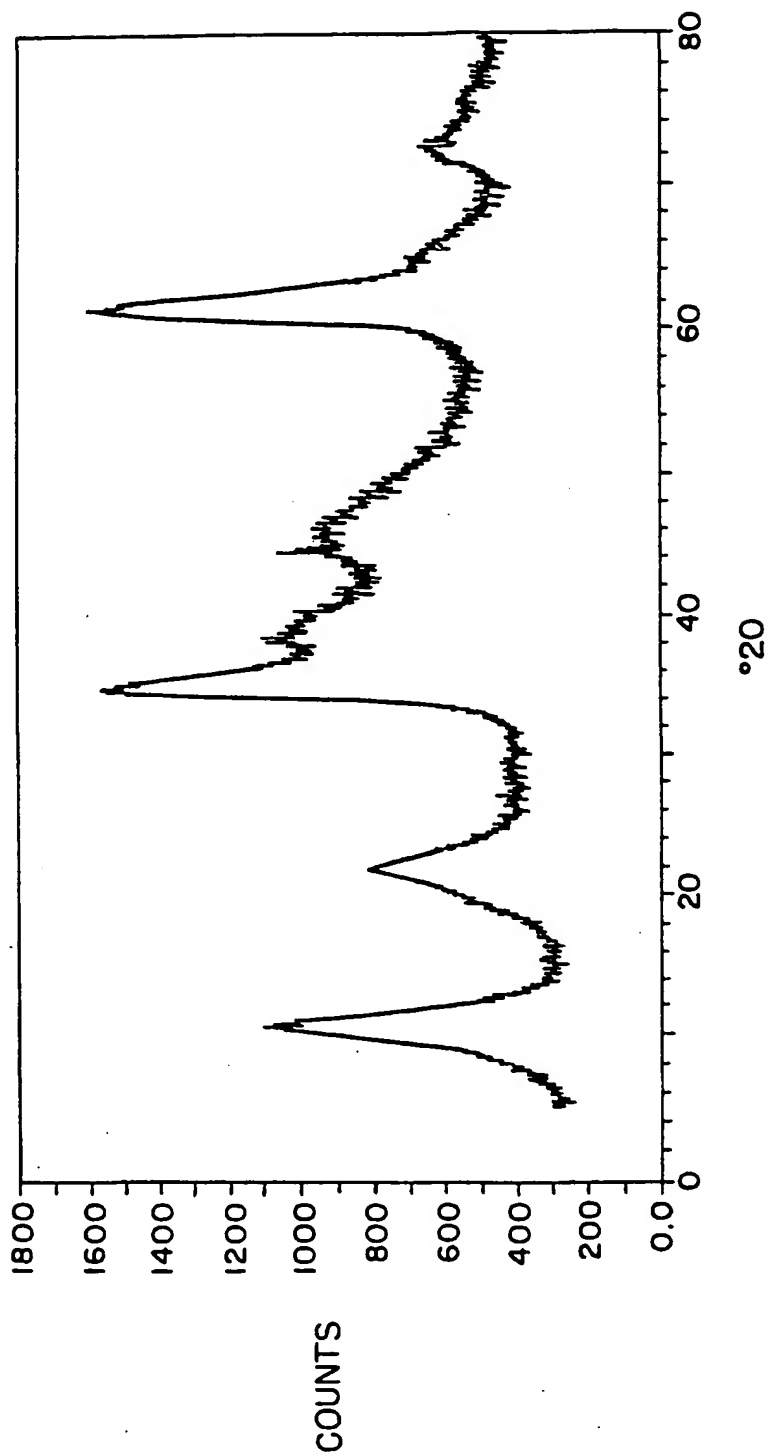
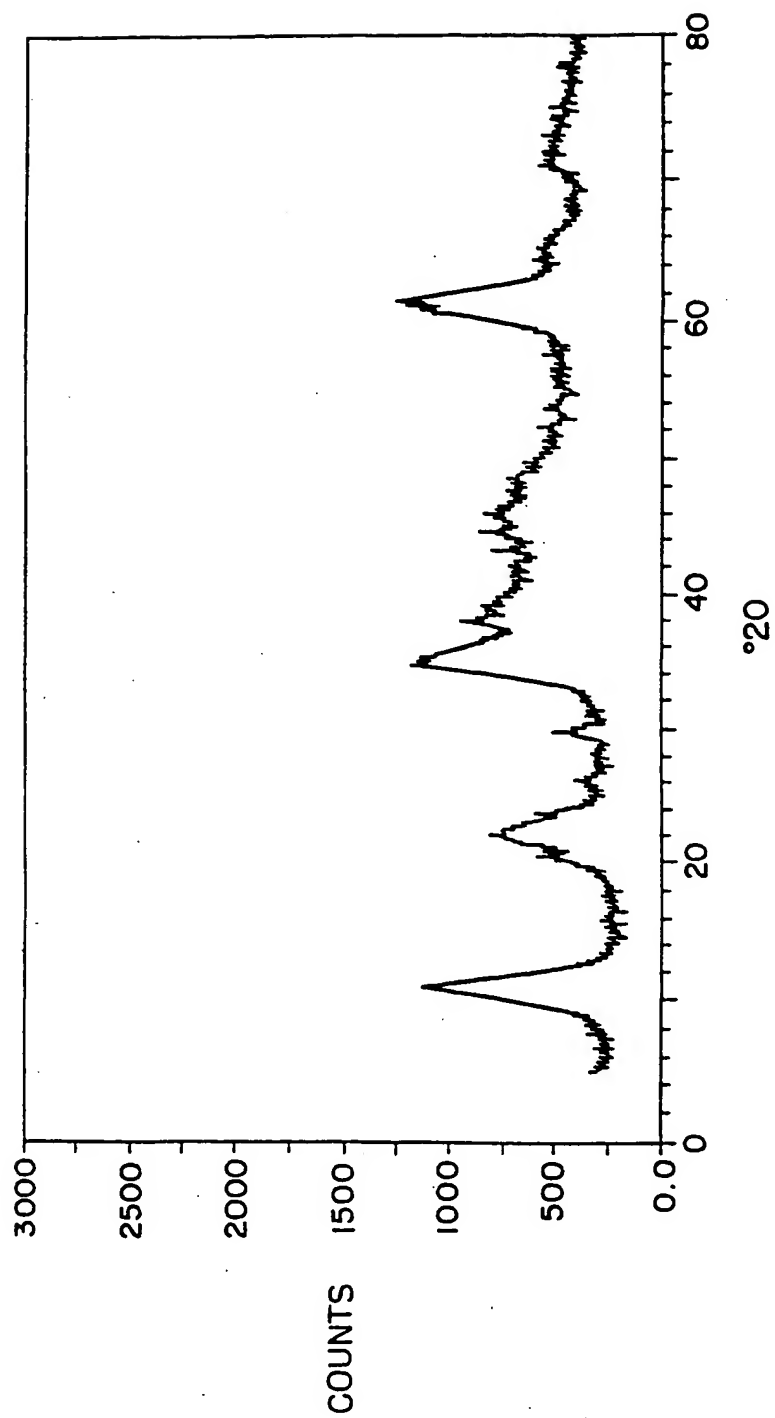
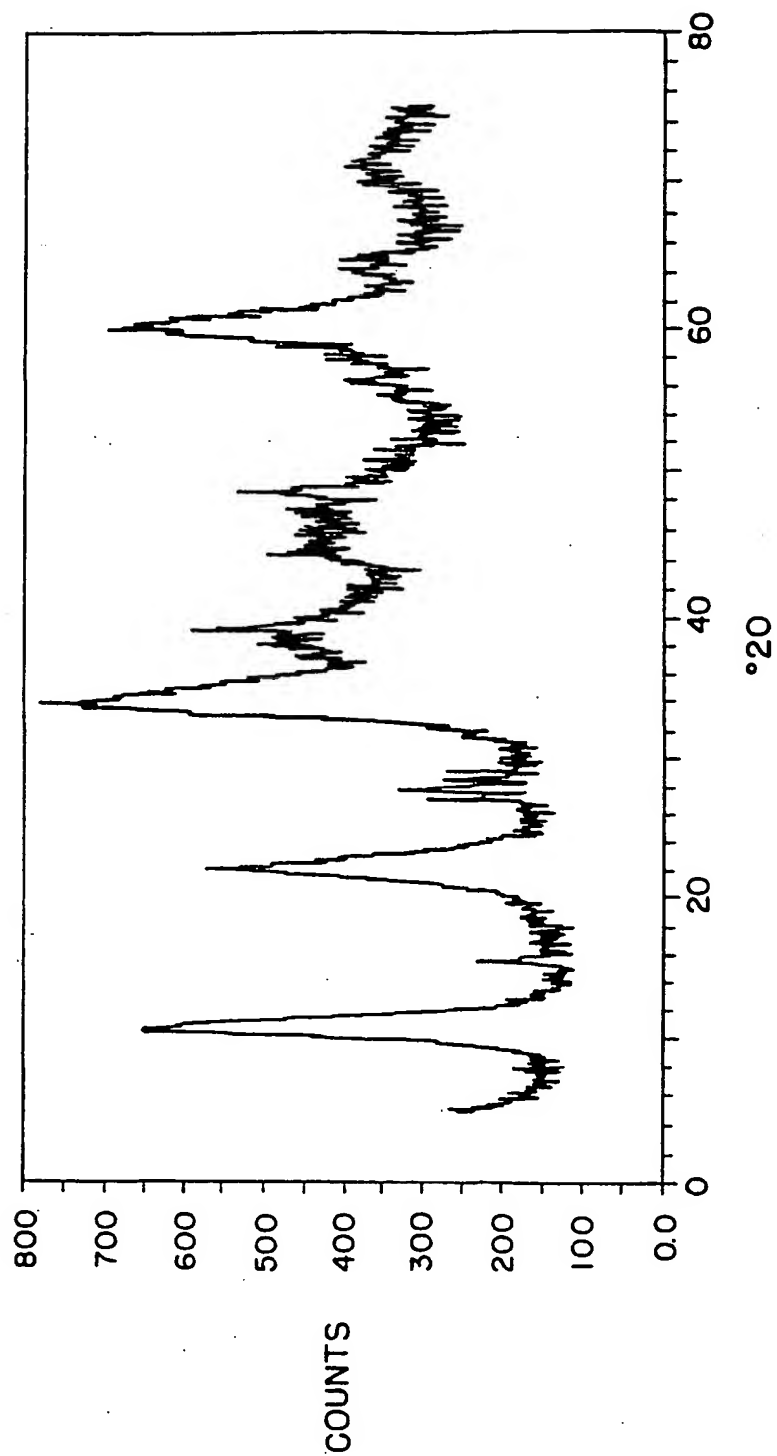


FIG. 5

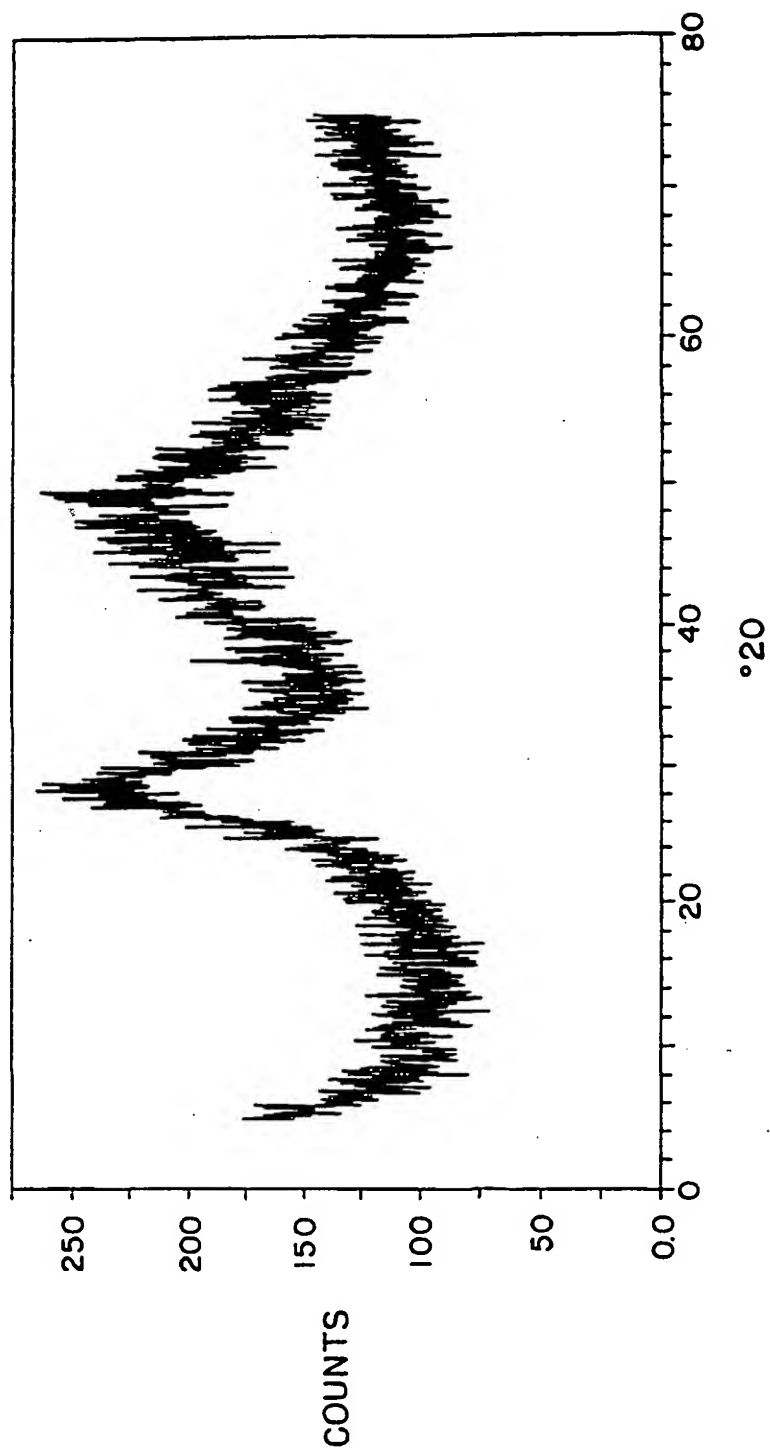
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**FIG. 6**

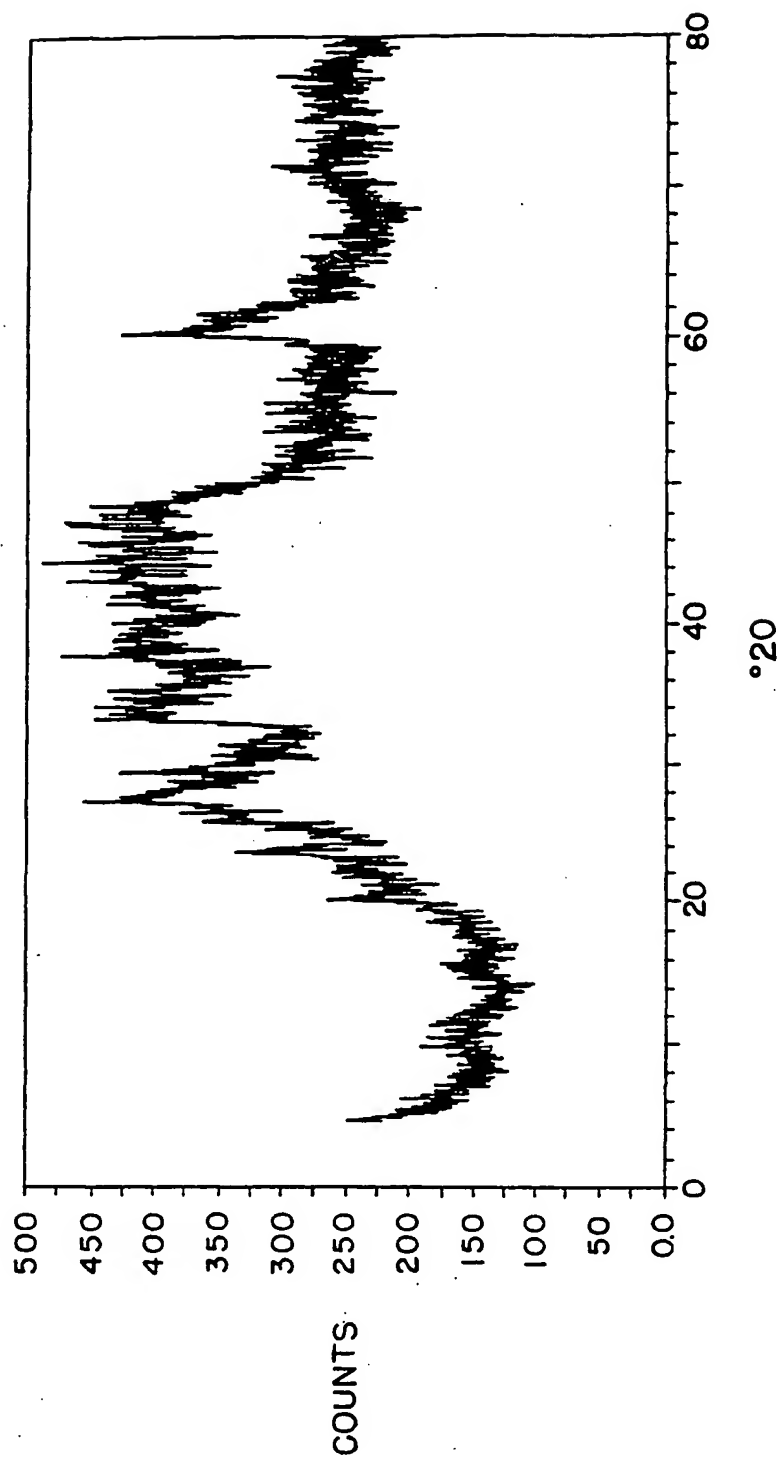
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*FIG. 7*

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*FIG. 8*

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*FIG. 9*

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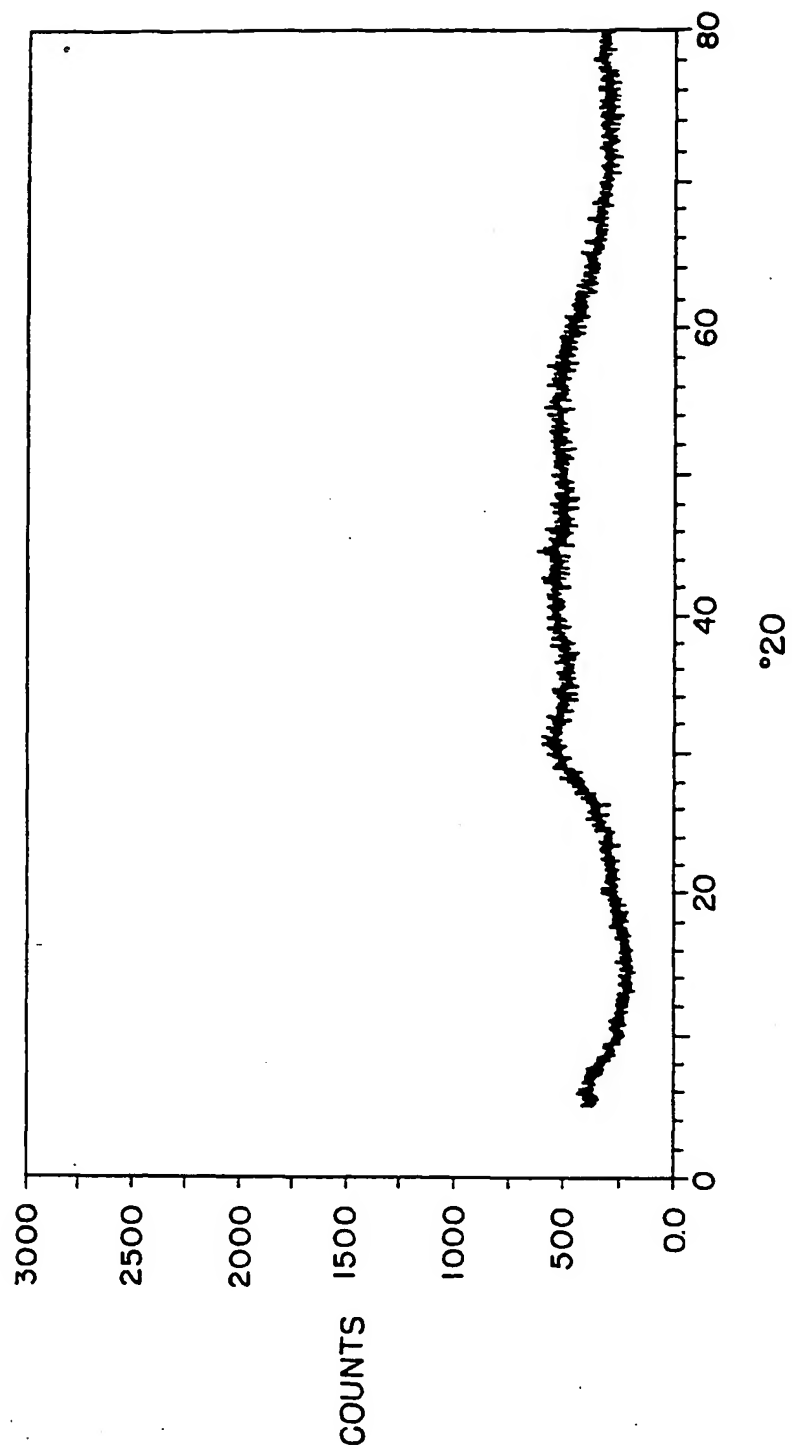


FIG. 10

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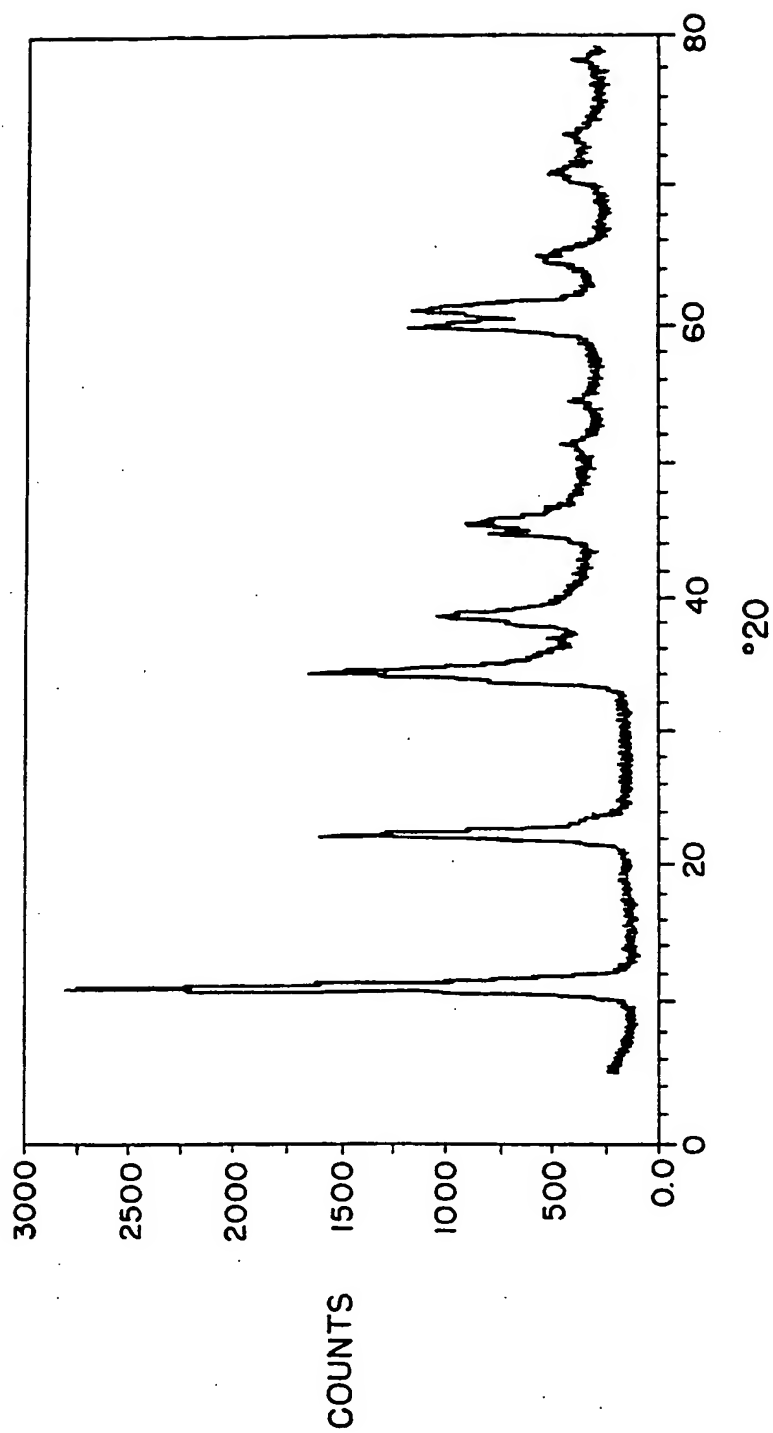


FIG. 11

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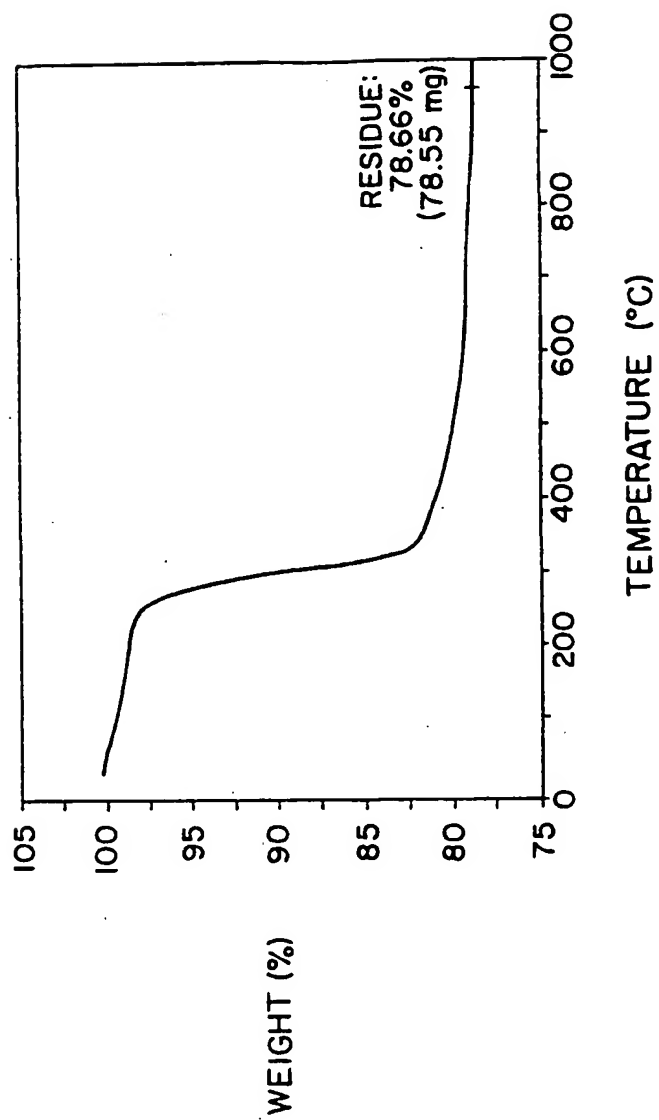


FIG. 12

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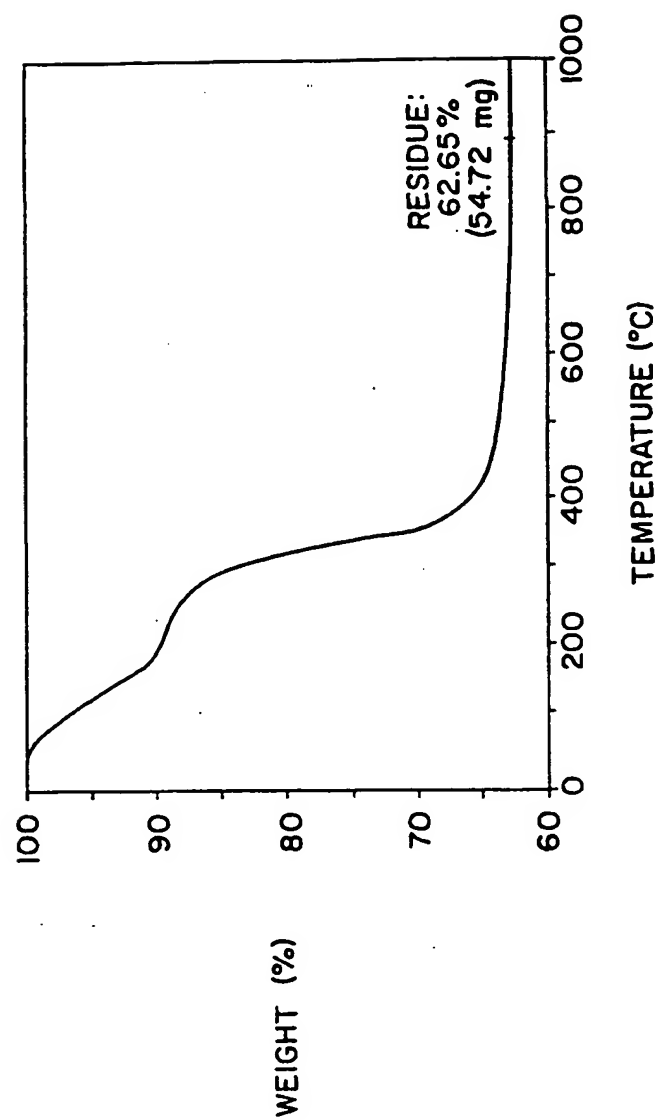


FIG. 13

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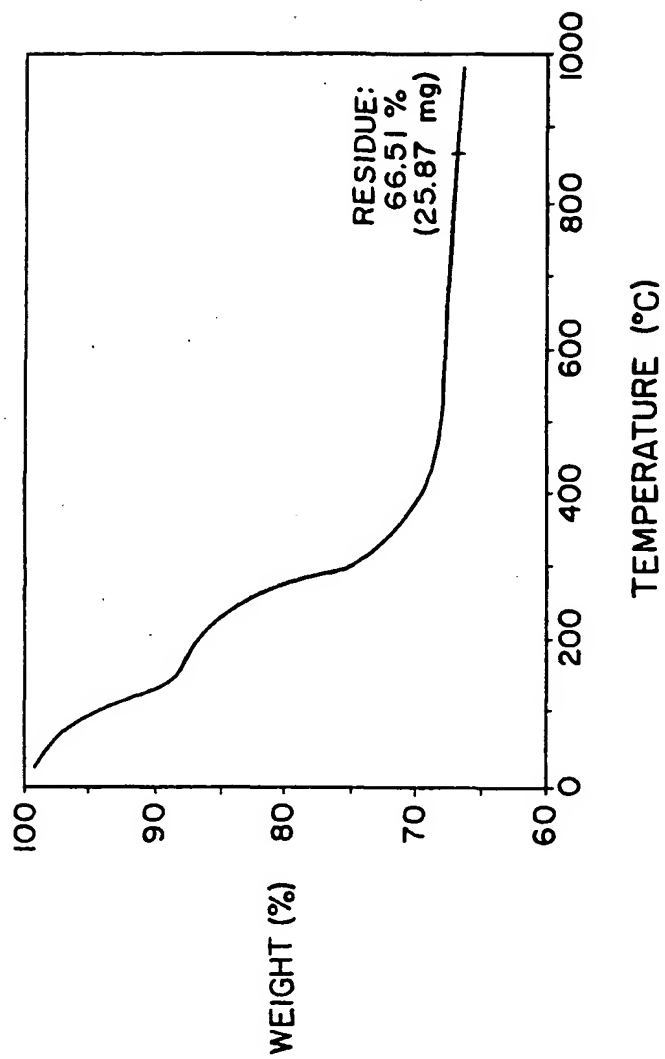


FIG. 14

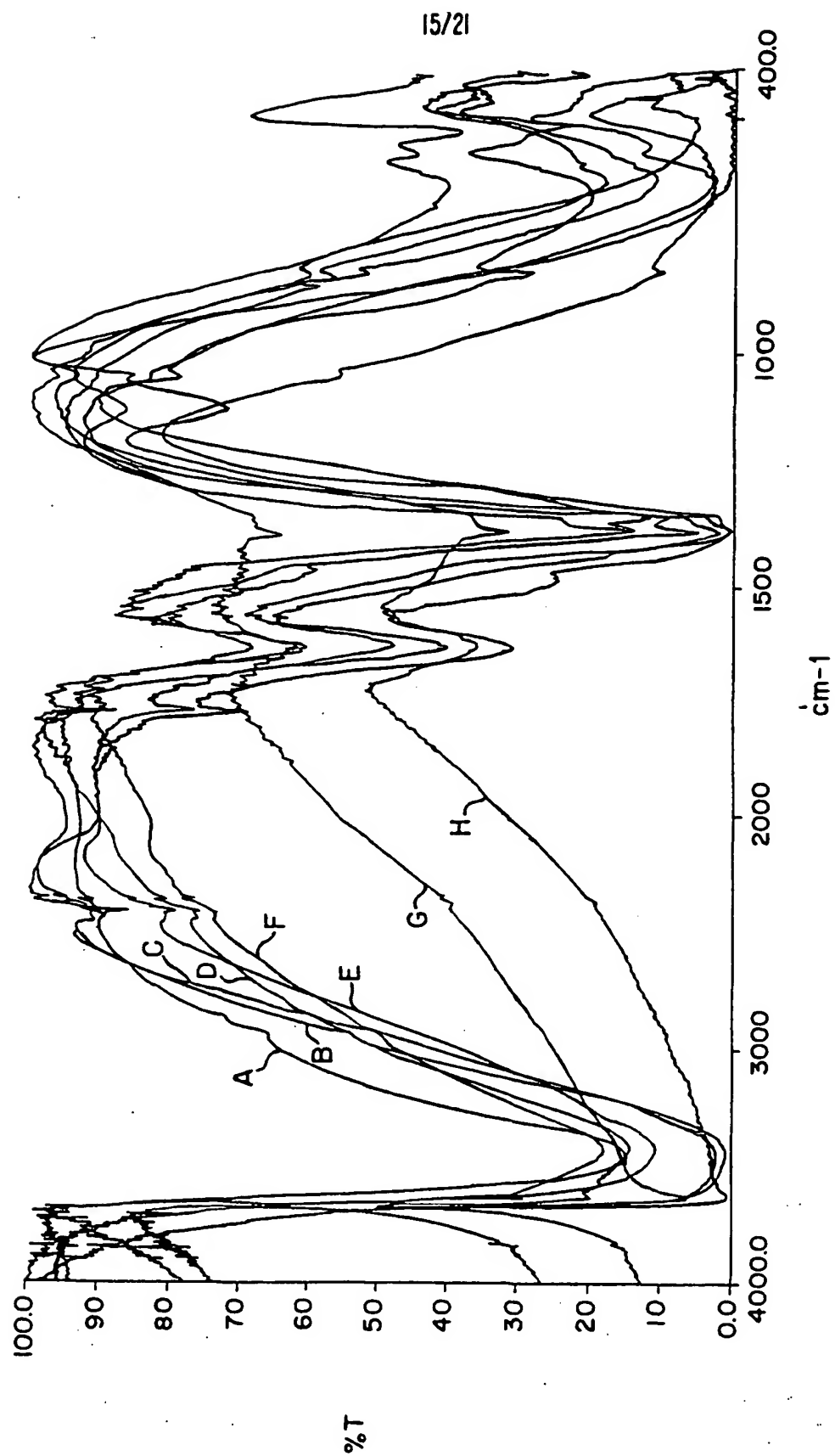


FIG. 15

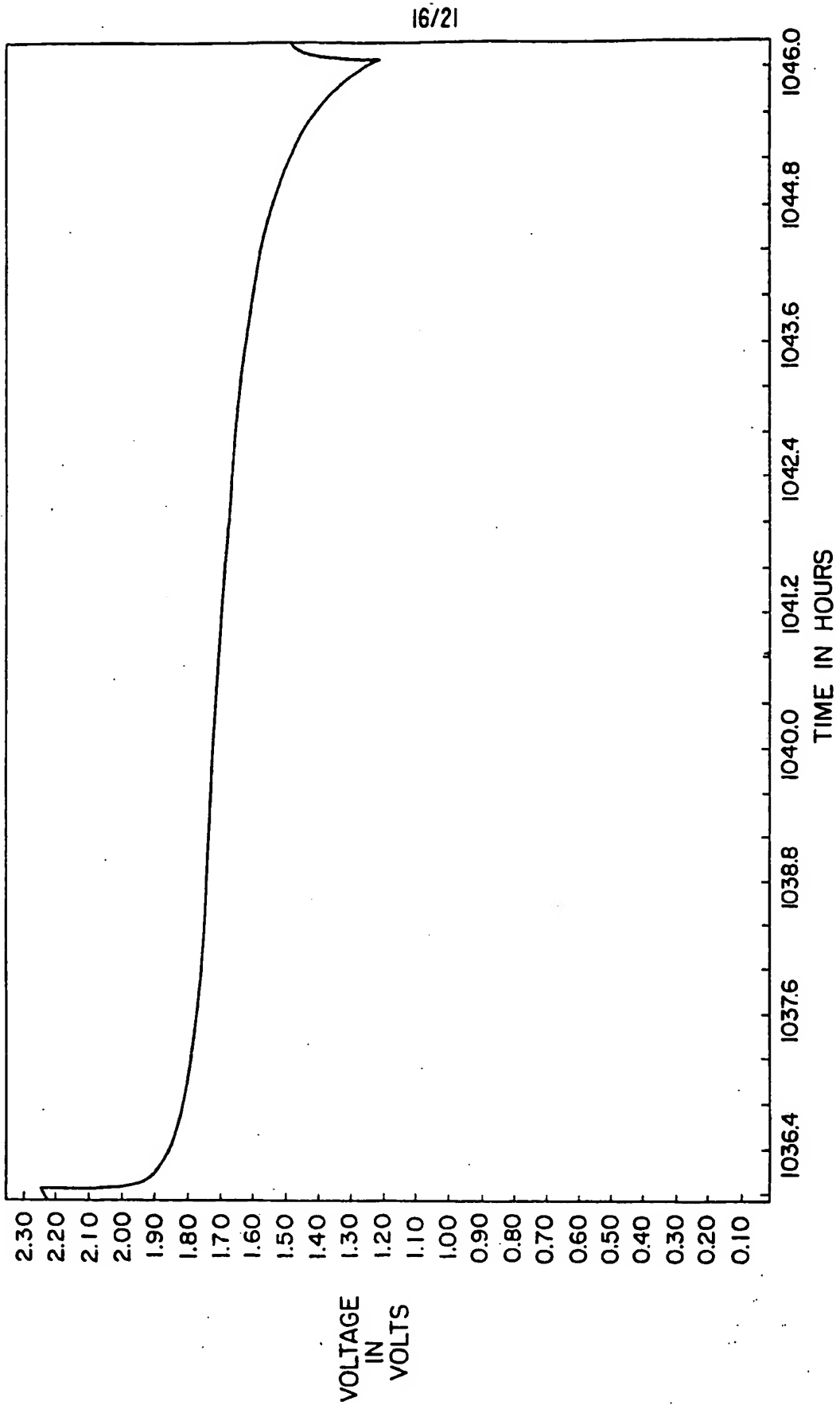
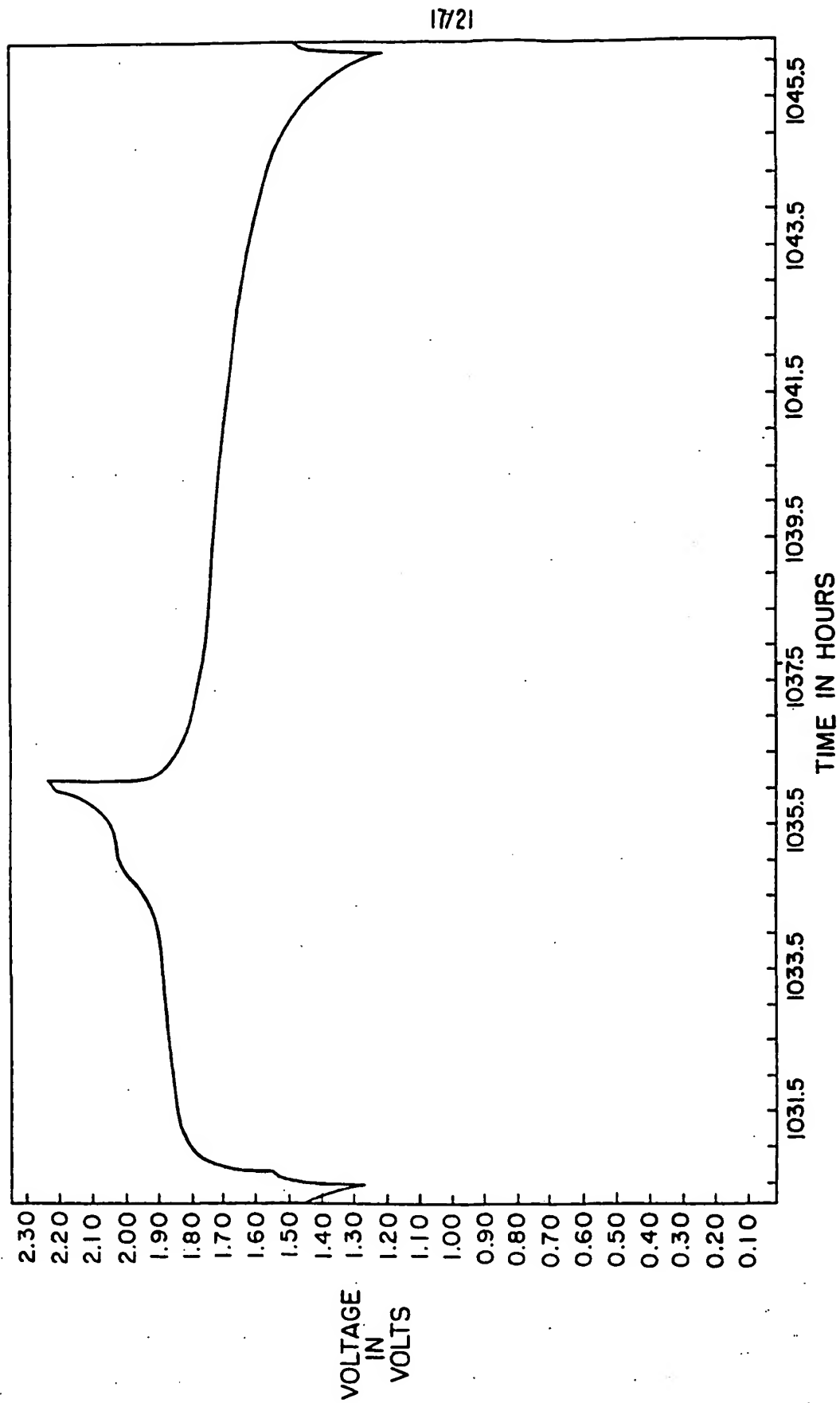


FIG. 16

**FIG. 17**

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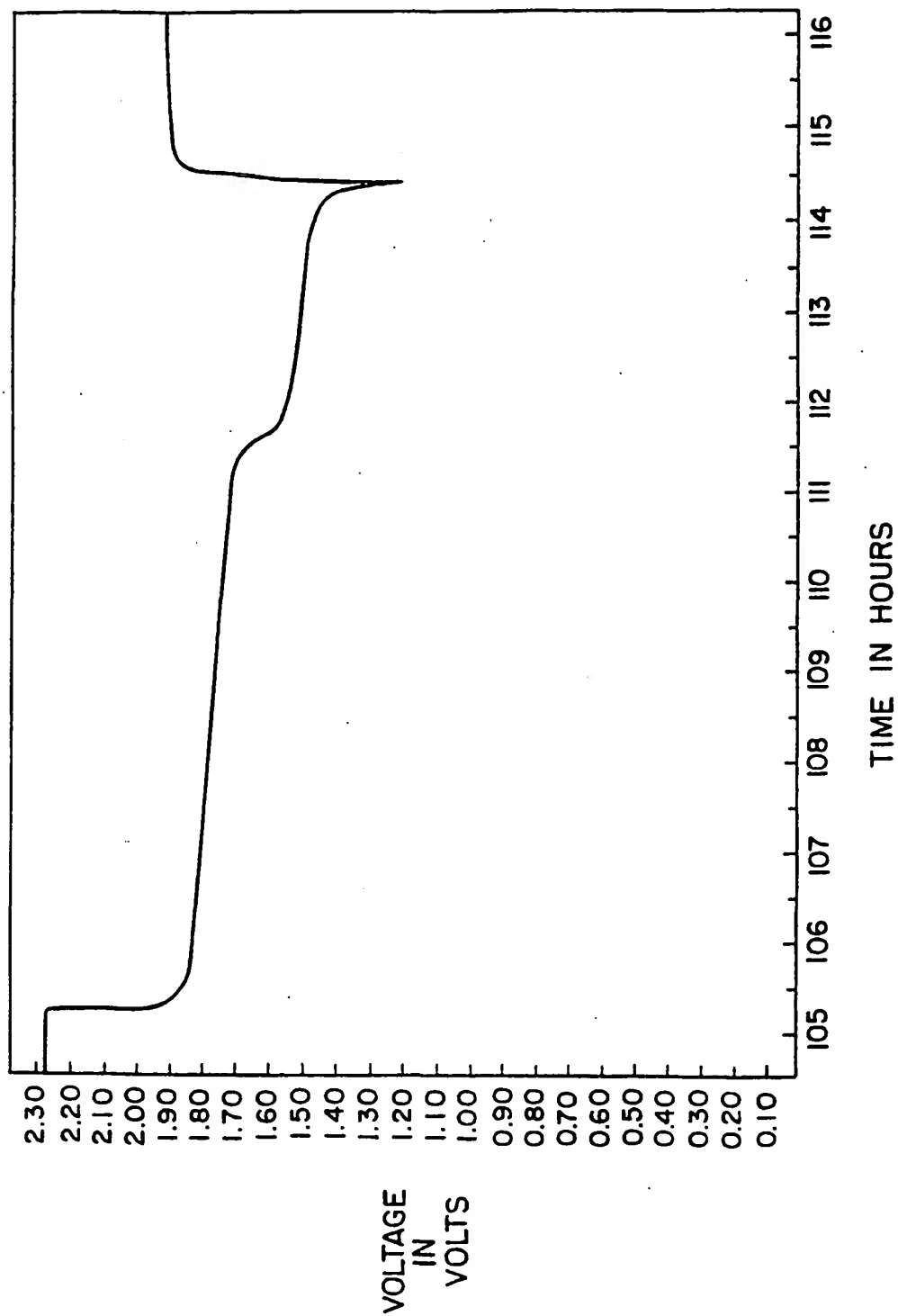


FIG. 18

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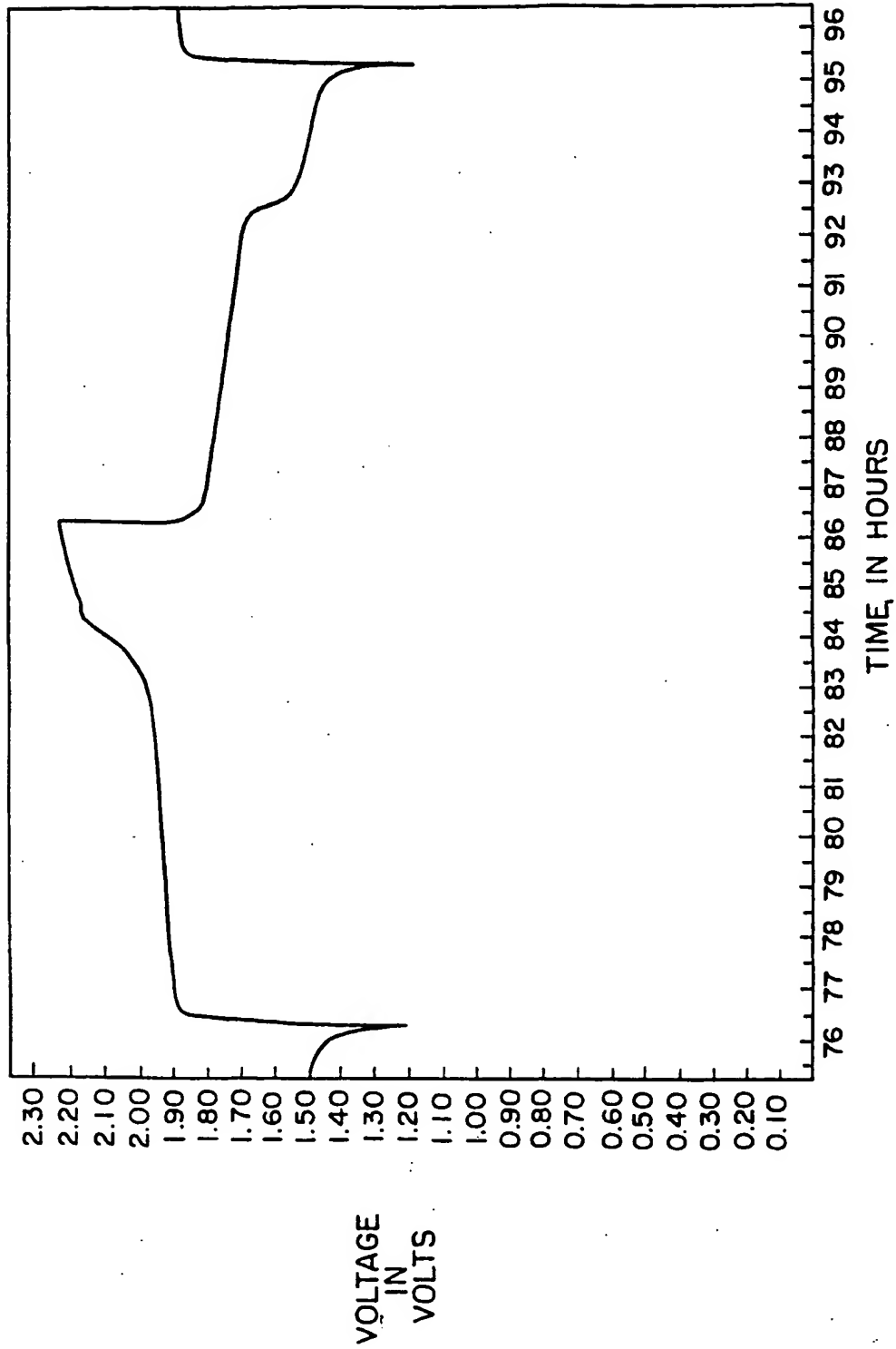


FIG. 19

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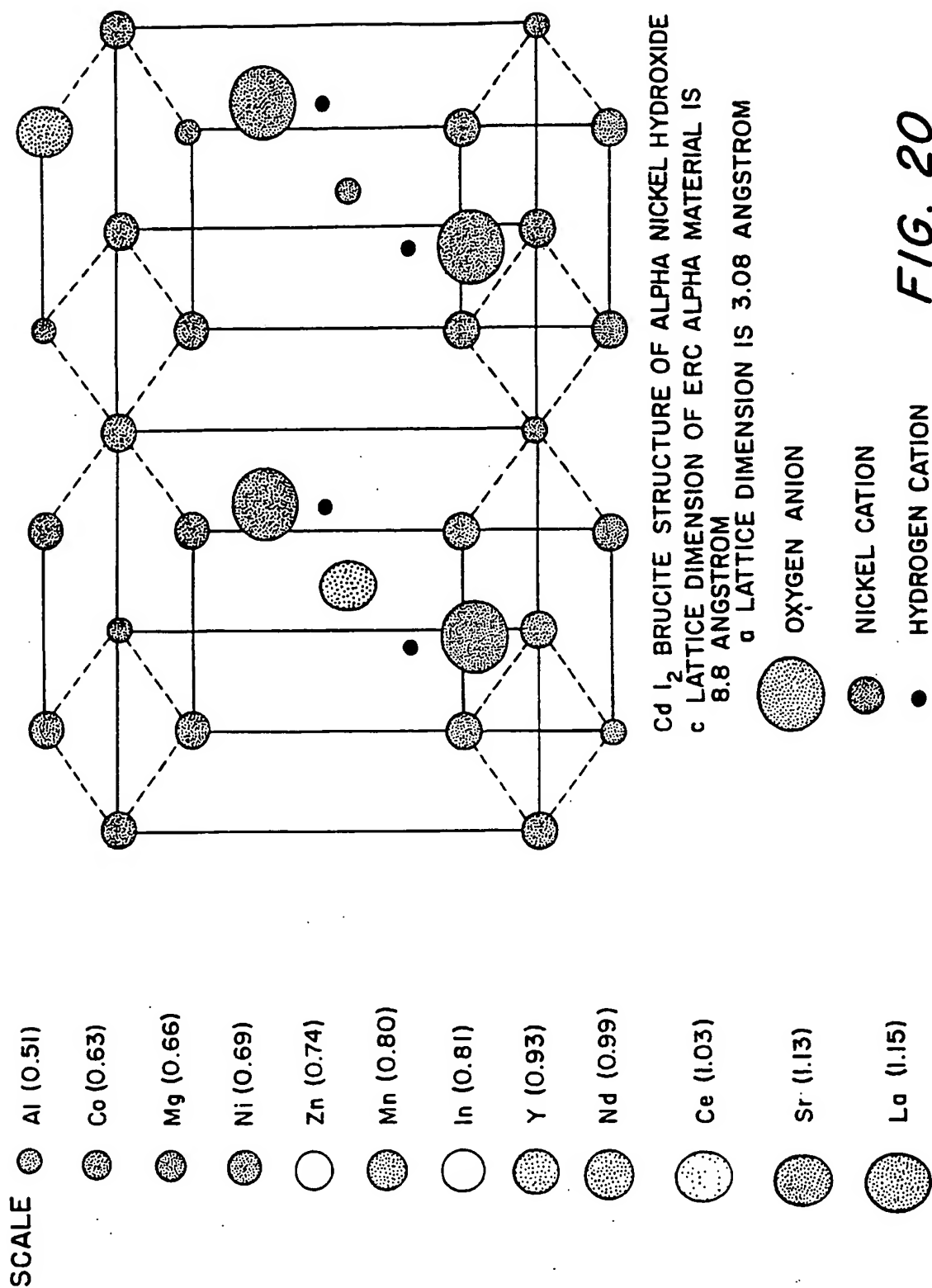
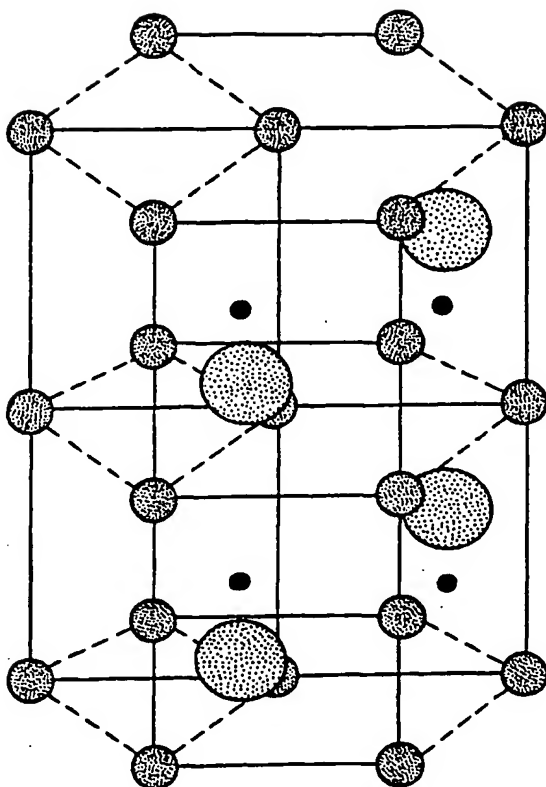


FIG. 20

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CdI_2 BRUCITE STRUCTURE OF STANDARD COMMERCIAL
BATTERY GRADE BETA NICKEL HYDROXIDE
c LATTICE DIMENSION IS 4.6 ANGSTROM
a LATTICE DIMENSION IS 3.12 ANGSTROM



OXYGEN ANION



NICKEL CATION



HYDROGEN CATION

FIG. 21

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/18782

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :H01M 4/32, 4/26
US CL :429/223.; 423/592, 594

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/223.; 423/592, 594

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST (USPAT, JPO, EPO)
search terms: nickel hydroxide, ni(oh)2, alpha

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,567,549 A (OVSHINSKY et al.) 22 October 1996, col. 7, lines 30-60; col.9, lines 1-65.	1, 12, 15 ----- 2-11, 13-14
X,P ----- Y, P	US 5,861,225 A (CORRIGAN et al.) 19 January 1999, col. 9, lines 7-12; Example II, Table 2, Example III, Table 3, Example V, Table 5.	1, 12, 15 ----- 2-11, 13-14
Y	US 4,546,058 A (CHARKEY et al.) 08 October 1985, col. 1, lines 11-14; col. 2, lines 59-64.	13, 14

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 20 OCTOBER 1999	Date of mailing of the international search report 29 NOV 1999
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer JENNIFER O'MALLEY Telephone No. (703) 308-0661 DEBORAH THOMAS PARALEGAL SPECIALIST

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/18782

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GENIN et al., Preparation and Characterization of alpha-Type Nickel Hydroxides Obtained by Chemical Precipitation: Study of the Anionic Species, Eur. J. Solid State Inorg. Chem, 1991, 28, pages 505-518, especially pages 506-507, 516.	2-11
Y	US 5,789,113 A (JOO et al.) 04 August 1998, col. 3, line 33 to col. 4, line 37; col. 5, lines 11-67.	2-11
Y	EHLSISSEN et al., Preparation and Characterization of Turbostratic Ni/Al Layered Double Hydroxides for Nickel Hydroxide Electrode Applications, J. Mater. Chem. 1993, 3(8), pages 883-888, especially pages 883, 886.	2-11
Y	DELMAS et al., The Effect of Cobalt on the Chemical and Electrochemical Behavior of the Nickel Hydroxide Electrode, 1992, pages 89-96	2-5, 6
A	US 5,670,271 A (AXMANN) 23 September 1997.	1-15